Development of a Zero-Emission Process for Electroplating Operations

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A major problem associated with chromium electroplating is the emission of hexavalent chromium, a known carcinogen, from the plating baths in the form of liquid aerosols formed by the surface impingement and breakage of air bubbles. Air sparging is used to maintain the bath temperature and mix the chromic acid in the plating bath. In this paper, a unique liquid formulation has been developed that spreads as a thin layer on the chromic acid liquid surface to prevent the formation and emission of aerosols and the transport of chromium into the air. Experimental studies have been conducted with the liquid formulation to demonstrate the quality of the plating, its non-adherence to plating parts, and its non-inteference with the plating process. Results of these studies and the development of a mathematical model to define the heat and mixing characteristics of the liquid formulation will be discussed in this paper.

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Dr. Rakesh Govind Department of Chemical Engineering Mail Location 171 University of Cincinnati Cincinnati, OH 45221-0171 Tel: (513) 556 2666 Fax: (513) 556 3473 Email: *rgovind@alpha.che.uc.edu* Hard chromium plating is extensively used in the industry to improve the wear characteristics of metal parts. It is also used for decorative purposes. EPA has identified hexavalent chromium, used in chromium plating, as one of the 17 high-priority toxic chemicals and is known to be a human carcinogen^{1,2}. It has been classified by the U.S. EPA as a Group A carcinogen³. Inhalation is the major exposure pathway for Cr⁶⁺. Workplace exposure to Cr⁶⁺ has been associated with a number of sources – metal plating, spray painting, welding, tanning, and abrasive blasting operations. As part of National Emission Standard for Hazardous Air Pollutants (NESHAP) the U.S. EPA has set the regulatory limits in micrograms per dry standard cubic meter at 15 and 30 μ g/dscm for stack concentrations for large and small hard chromium electroplating facilities, respectively. OSHA regulations require the Personal Exposure Limit (PEL) of 100 μ g/m³ and proposed exposure limit of 0.5 μ g/m³ with an action level of 0.25 μ g/m³.

Regulation of bath temperature and mixing of the plating solution are essential for successful electroplating. Reject rate of parts increases due to non-uniformity of temperature in the plating bath and this increases waste generation. Traditionally, temperature control and mixing have been achieved by bubbling air at the bottom of the plating bath using a sparger. When these air bubbles, together with the hydrogen and the oxygen evolved at the electrodes, break at the surface of the plating solution, they produce aerosols that are responsible for the chromium emissions. The proposed process, shown schematically in Figure 1, uses a fluid layer, immiscible with the plating solution, at the top of the plating solution to control the emissions.



Figure 1- Schematic of the Proposed Zero-Emission Process using a Liquid Layer to Eliminate Aerosol Emissions.

Mixing and heat transfer are achieved by sparging this fluid at the bottom of the plating bath. The liquid is physiologically inert, non-volatile, immiscible with the chromic acid solution, electrically non-conductive, and possesses density less than water. This proprietary liquid, named PRD-EL1, accomplishes the following in the proposed process: (1) mixing of the liquid bath to minimize concentration polarization at the electrodes and concentration gradients within the bath; (2) eliminate the breakage of the bubbles at the liquid surface, which create the liquid aerosols responsible for air emission of hexavalent chromium in the conventional process; (3) prevent the deposition of particulate matter on the plating surface; (4) maintain the bath temperature by

removing excess heat generated in the bath due to resistive heat losses; (5) prevent water evaporation; and (6) eliminate the need for air sparging, which requires expensive air handling equipment and generates liquid waste when the vented air is scrubbed with water to reduce chromium stack emissions.

Alternative Emission Control Technologies

Pollution control devices for chromium plating can be divided into two categories: Add-on pollution control devices and Chemical fume suppressants.

Add-on control devices

Add-on air pollution control device, as the name suggests, are installed in the ventilation system as an add-on to trap any escaping chromium. Add-on air pollution control devices are designed to capture the emission once it had been released from the electroplating bath. Some examples of the add-on devices are:

- Condensers
- Carbon absorbers
- Scrubbers
- Fabric filters

These units are placed on the exhaust stream from the process and have the advantage of requiring minimal changes in the process itself. Wet collectors (also called scrubbers) are the most commonly used pollution control devices for removing acid/alkali pollutants. Packed-bed scrubbers are the most efficient of the commonly used wet collectors. Although most scrubbers can readily achieve mist removal efficiencies of 90-99%, it is important to choose the proper scrubber to maximize its gaseous removal efficiency. Such devices, however, are often very expensive to purchase, operate and maintain, and can substitute one pollution problem (air) for another (contaminated water discharge or hazardous waste generation). The need for ventilating pipes and requirement of a discharge stack increases the cost of the system and the shop's ability to utilize all of the available space, since the gas ventilation pipes are usually placed along the outside walls of the building.

Chemical fume suppressants

The use of chemical fume suppressants is common in the plating industry. Chemical fume suppressant systems use wetting agents or foam blankets, or a combination of both. They are stable surface-active agents which reduce the emission of chromic acid by lowering the surface tension of the bath solution. The use of stable surface active agents as fume-suppressants is an easy way to reduce the environmental and workplace safety hazards associated with misting. It is known that lowering the surface tension causes the size of the bubbles to increase and hence reduction in the emissions. These agents act primarily by lowering the surface tension to reduce the size of evolved gas bubbles resulting in less solution travel when the bubbles break.

Surface agents invariably lead to the formation of a foam blanket on top of the bath. This blanket captures hydrogen bubbles and can be a potential hazard in presence of sparks from poor bus-bar-to-rack connections. Other cause of concern is that these foam blankets accumulate dirt and grease which can stick to the part while insertion into the tank and cause pitting.

Experimental Testing of the Proposed Process

Figure 2 shows the bench scale experimental setup designed to evaluate the proposed zero-emission process. A 2-liter Kimble jacketed beaker was used as the experimental tank, connected to a water bath to maintain

constant temperature in the beaker. The cathode and the anodes were connected to a power supply capable of delivering up to 30 A current at 8V.



Figure 2- Schematic of the Bench-Scale System to test the Zero-Emission Electroplating Process.

Parts of three levels of difficulty of plating were designed, Type A – the easiest to plate, Type B – parts with moderate difficulty of plating, and Type C – parts most difficult to plate. Figure 3 shows the three types of parts which were plated in the bench-scale process.



Figure 3- Drawing showing the Three types of Parts which were Plated during the Bench-Scale Testing.

Type A has both sides of the flat sheet accessible by the electrodes. Type B has a common edge, which is discontinuity and Type C has an interior surface that has to be plated.

Results and Discussion

Tests were conducted to evaluate the quality of the hard chromium plating obtained using the conventional and the zero-emission process. Parts of varying degree of difficulty of plating were plated and compared. OSHA Method ID 215 analysis was used for the detection of Cr(VI) in the workplace environment. The quality of the finish was compared based on two tests: *Scratch Adhesion Test*, and *Pit Counts*.

Scratch Adhesion Tests

Scratch adhesion testing is performed on a coated sample to measure the critical load at which a coating shows signs of failure. The test can be performed with varying table speed, load rate, initial load and final load. The friction force is recorded and displayed during the scratch test.

The adhesion between the coating layer and the substrate and the critical force, at which the coating fails, were examined by using a *Sebastian V Scratch Tester* (Quad Group, Spokane, WA). The coated sample is positioned underneath the diamond. Loading rates and speeds may be left at a default setting or can be fully defined by the user through the computer. The table-drive speed, rate of loading, initial load and final load are selected by the user.

The *sample stage* moves horizontally along with the sample at a predetermined scanning rate. An increasing normal load, starting from zero, is applied on the *stylus* (diamond tip with a 533 µm in radius) at a predetermined loading rate. Each sample was scratched three times. Computer logged-data obtained from the scratch test include *applied load, transverse force, friction coefficient, and acoustic emission signal*, which is detected by a piezoelectric acoustic transducer mounted on the *stylus arm*. The acoustic noise generated during the scratch test is recorded in order to identify the critical force. A burst in the acoustic signal indicates either debonding or cracking of the coatings.

The scratch tracks on the films were examined by using an optical microscope. During the scratch test, the scan and loading rates were maintained at 0.04 cm sec⁻¹ and at 0.03 kg sec⁻¹, respectively. The maximum load and travel distance were fixed at 4 kg and at 3 cm, respectively.

The results of the tests are shown below in Figures 4 through 12 for Types A, B, and C parts. Besides experimental scatter, there is no difference in the critical load, traverse force and friction coefficient of the parts plated using conventional process and the zero-emission process.



Figure 4- Critical Load (kg) for Type A part using Conventional & Zero-Emission Plating Processes.



Figure 5- Critical Load (kg) for Type B part using Conventional & Zero-Emission Plating Processes.



Figure 6- Critical Load (kg) for Type C part using Conventional & Zero-Emission Plating Processes.



Figure 7- Transverse Force (kg) for Type A part using Conventional & Zero-Emission Plating Processes.



Figure 8- Transverse Force (kg) for Type B part using Conventional & Zero-Emission Plating Processes.



Figure 9- Transverse Force (kg) for Type C part using Conventional & Zero-Emission Plating Processes.



Figure 10- Friction Coefficient for Type A part using Conventional & Zero-Emission Plating Processes.



Figure 11- Friction Coefficient for Type B part using Conventional & Zero-Emission Plating Processes.



Figure 12- Friction Coefficient for Type C part using Conventional & Zero-Emission Plating Processes.

Pit Counting Analysis

Pit count is the count of number of pits on the surface per unit area. The pit count measurements were made using SEM scans of the surface. S4000 Field Emission Gun (FEG) Scanning Electron Microscope (SEM) manufactured by JOEL Inc. was used to obtain the surface scans of the Cr(VI) coated parts. It has resolution of

20 Å. It is equipped with an Oxford Isis Energy Dispersive Spectroscopy system including a light element detector and digital imaging, an Oxford Solid-State BSE detector and an Oxford Opal Backscattered Diffraction Pattern System for crystallographic analysis.

The plated surface was scanned down to 0.1 μ m resolution, 30,000X magnification. The surface scans show no sign of pit formation on the surface.

Emission Analysis

The zero-emission process did not produce any aerosol emissions of chromium, as measured by the OSHA method. All the filters had non-detectable levels of hexavalent chromium.

Conclusions

A zero-emission electroplating process has been developed which involves a specially formulated liquid layer on the liquid surface of the electroplating tank. The liquid is recycled to provide mixing of the liquid in the tank and is cooled using an external heat exchanger to maintain the tank temperature. The liquid droplets provide mixing of the liquid in the tank, prevent deposition of particulates on the plating surface and minimize the effect of concentration polarization at the electrodes. The main benefits of the zero-emission process are (1) zero emission of liquid aerosols, primarily responsible for the emission of hexavalent chromium from electroplating tanks; (2) prevent corrosion by the chromic acid at the tank-liner interface; (3) prevent accumulation of hydrogen gas, as in the case of foam; (4) improved temperature control, which results in better quality of plating; (5) no evaporation of water from the tank, when no electroplating is being conducted, thereby preventing the addition of make-up water; and (6) achievement of plating quality which is as good as with the conventional plating process, based on the scratch test and pit counts on the surface. The zero-emission system can be easily retrofitted to any electroplating tank and results in considerable savings in investment cost since no air ventilation system is required and operating costs due to reduced space heating charges in the winter time in cold climate locations.

References

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